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FOURTH QUARTERLY STATUS REPORT
July 1, 1962-September 30, 1962

to

Director, Manned Spacecraft Center
National Aeronautics and Space Administration
Houston 1, Texas

Contract No. NASr-70

ELECTROLYTIC PRODUCTION OF OXYGEN
AND
REDUCTION OF CARBON DIOXIDE

C. A. Palladino
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October 15, 1962

MSA Research Corporation

Subsidiary of Mine Safety Appliances Company

Callery, Pennsylvania

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Job No. XAC-720291

October 15, 1962

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ABSTRACT

Current work is with organic solvents and cation exchange membranes in an effort toward finding a workable system for cathodic reduction of carbon dioxide with concurrent anodic production of breathing oxygen. Several systems using an electrolyte of lithium chloride at a lead cathode produced some carbon monoxide and methane. However, blank runs strongly indicated these products to be from solvent reaction and not carbon dioxide reduction. Results to date have been negative.

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Fourth Quarterly Status Report

on

ELECTROLYTIC PRODUCTION OF OXYGEN AND REDUCTION OF CARBON DIOXIDE

INTRODUCTION

This is the Fourth Status Report on Contract No. NASr-70 for July, August and September 1962. The object of this work is the continuous cathodic reduction of CO_2 with concurrent anodic production of breathing oxygen.

The experimental approach is to evaluate the products of electrolysis cells. Some of the variables being studied are cathode materials, electrolytes, temperature, pressure and cell geometry. During this report period work has centered on ion exchange membrane-organic solvent combinations.

EXPERIMENTAL PROCEDURES AND RESULTS

Experimental Cells

Except for a series of conductivity tests in a beaker cell, the glass pipe pressure cells were used for all the reduction experiments performed during this report period. This type cell, described in a previous Status Report,¹ is well suited to the experiments using organic solvents for the catholytes, a non-rigid cation exchange membrane, and an aqueous 10% sulfuric acid anolyte. When a porous alundum cup was used as the diaphragm, the cells were operated with oxygen pressure at the anode, and carbon dioxide at the cathode; but with the use of a non-rigid membrane it was necessary to maintain equal pressure on both sides of the cells at all times. To avoid membrane rupture caused by pressure fluctuations both sides of the cell were pressurized with CO_2 and connected with an equalizer line. This resulted in some mixing of the gas phase products of the electrolysis. Blank cells were run when there was doubt as to the origin of electrolysis products. The blank cells were run at the same conditions as the original cells but were pressurized with helium instead of carbon dioxide.

Attempts were made to set up an automatic gas pressure control system using differential pressure switches and solenoid valves. This would allow unattended operation of the cells and separation of the anode and cathode gas electrolysis products. The initial set-up resulted in a ruptured cation exchange membrane because of a leak in a check valve. This will be tried again with a different type check valve.

Cathode Material

The cathodes used for the organic solvent systems, except for two runs, were oxidized lead rods. The lead rods were prepared by a modification of the Tafel method.² The lead rod was placed in a 20% solution of H_2SO_4 and surrounded by a lead sheet. The lead rod was used as the anode at a current density of 0.02 amp per cm^2 . After five minutes the polarity was reversed and the lead rod was reduced for five minutes. The cycle was repeated a second time. The lead rod was left in the oxidized condition by an additional five minute electrolysis as the anode.

Organic Catholyte Solvents

The organic catholyte solvents were chosen because of previous performance in the literature as being solvents for the electrodeposition of beryllium and lithium. Several workers electroplated Be from ethereal solutions of $BeCl_2$.³ Lithium has been deposited from acetone^{4,5} and pyridine.⁶

The catholytes were prepared by placing the catholyte salt to be used in a 500 ml flask and adding the organic. The mixture was stirred overnight in order to insure saturation. The catholyte was then transferred to the cathode compartment of a glass pressure cell along with some solid electrolyte to insure maximum saturation.

Electrolytic Reduction Experiments

Table 1 is a summary of the conditions and results of the experiments conducted during this report period. Except as noted in the table, all data under the column head "tests" refer to the cathode gas or catholyte.

A series of tests using bis-2-dimethoxyethyl ether with Li_2SO_4 , $LiCl$, $NaNO_3$, $BeCl_2$ and K_2CO_3 (Runs 159a-159k) showed no conductance with or without CO_2 passing through the solution.

TABLE 1 - SUMMARY OF REDUCTION RUNS

Run	Type of Cell	Dimensions	Anode	Anolyte	Diaphragm	Cathode	Catholyte	Time
159 (a)	Beaker	2 1/2" Diam.	Pt. disc	(organic) bis-2-dimeth- oxyethyl ether + LiSO ₄	None	Pt disc	(organic) bis-2-dimeth- oxyethyl ether + LiSO ₄	0
(b)	"	"	"	"	"	"	+ CO ₂	0
(c)	"	"	"	+ LiCl	"	"	+ LiCl	0
(d)	"	"	"	"	"	"	+ CO ₂	0
(e)	"	"	"	+ NaNO ₃	"	"	+ NaNO ₃	0
(f)	"	"	"	"	"	"	+ CO ₂	0
(g)	"	"	"	+ Na ₂ CO ₃	"	"	+ Na ₂ CO ₃	0
(h)	"	"	"	"	"	"	+ CO ₂	0
(i)	"	"	"	+ BeCl	"	"	+ BeCl ₂	0
(j)	"	"	"	"	"	"	+ CO ₂	0
(k)	"	"	"	+ K ₂ CO ₃	"	"	+ K ₂ CO ₃	0
160	2" Glass Pipe	8" center	Pt. wire	10% H ₂ SO ₄	2 cation ex- change mem- branes (N)	Hg	BeCl ₂ -ether + CO ₂	22 hrs.
161	"	"	"	"	" (N)	Hg	BeCl ₂ -ether H ₂ O + CO ₂	7 hrs.
162	"	"	Pt sheet	10% H ₂ SO ₄ 40 psig CO ₂	cation ex- change mem- brane (N)	Oxidized lead rod	LiCl-acetone 40 psig CO ₂	17 hrs.
163	"	"	"	"	" (N)	"	LiCl-acetone 40 psig CO ₂ 0°C	8 hrs. 2 hrs. 3 hrs.
164	"	"	"	10% H ₂ SO ₄ 20 psig CO ₂	" (N)	"	LiCl-acetone 20 psig CO ₂ 75°C	6 hrs.
165	2" Glass Pipe	8" center	Pt sheet	10% H ₂ SO ₄ 40 psig He	cation ex- change mem- brane (N)	Oxidized lead rod	LiCl-acetone 40 psig He	9 hrs.
166 (a)	2" Glass Pipe	8" center	Pt sheet	10% H ₂ SO ₄ 30 psig CO ₂	cation ex- change mem- brane (N)	Oxidized lead rod	LiCl-anisole 30 psig CO ₂	0
(b)	"	"	"	"	"	"	Li ₂ SO ₄ -anisole 30 psig CO ₂	0
(c)	"	"	"	"	"	"	NaCl-anisole 30 psig CO ₂	0
(d)	"	"	"	"	"	"	Na ₂ SO ₄ -anisole 30 psig CO ₂	0
(e)	"	"	"	"	"	"	MgSO ₄ -anisole 30 psig CO ₂	0
167	2" Glass Pipe	8" center	Pt sheet	10% H ₂ SO ₄ 40 psig CO ₂	cation ex- change mem- brane (N)	Oxidized lead rod	LiCl-Pentanone 40 psig CO ₂	46 hrs.
168	2" Glass Pipe	8" center	Pt sheet	10% H ₂ SO ₄ 40 psig CO ₂	cation ex- change mem- brane (I)	Oxidized lead rod	LiCl-Pyridine 40 psig CO ₂	27 hrs.
169 (a)	2" Glass Pipe	8" center	Pt sheet	10% H ₂ SO ₄ 40 psig CO ₂	cation ex- change mem- brane (I)	Oxidized lead rod	LiCl-Aceto- Nitrile 40 psig CO ₂	18 hrs.
(b)	"	"	"	10% H ₂ SO ₄ 40 psig He	"	"	LiCl-Aceto- Nitrile 40 psig He	19 hrs.
170	2" Glass Pipe	8" center	Pt sheet	10% H ₂ SO ₄ 40 psig CO ₂	cation ex- change mem- brane (I)	Oxidized lead rod	LiCl-Propylene carbonate	52 hrs.
171	U-tube	2 1/2" center	Pt sheet	MgSO ₄ -ether	None	Pt sheet	MgSO ₄ -ether	0

N = Cation exchange Nepton CR-61

I = Cation exchange IONAC MC 3142

<u>Amp.</u>	<u>Volts</u>	<u>Tests</u>	<u>Remarks</u>
0	48		Cell would not conduct
0.	48		" " " "
0.0003	48		
0.0003	48		
0.0003	48		
0.0003	48		
0	48		Cell would not conduct
0	48		" " " "
0.0005	48		
0.0005	48		
0	48		Cell would not conduct
0.002	47	HCHO, HCOOH, CH ₃ OH, Neg.	
0.1	47	HCHO, HCOOH, CH ₃ OH, Neg.	
0.5	48	HCHO Neg., 400 ppm CH ₄ 0.7% CO	
0.15	24	CH ₄ Neg. CO trace	Cell at 0°C
0.5	42	CH ₄ 75 ppm, CO 0.28%	
1.0	42	CH ₄ 150 ppm, CO 0.35%	
0.5	17	CH ₄ 150 ppm, CO 150 ppm	Cell at 75°C Membrane ruptured
0.5	48	CH ₄ 150 ppm, CO 440 ppm	Blank run
0	48		Cell would not conduct
0	48		" " " "
0	48		" " " "
0	48		" " " "
0	48		" " " "
0.003	48	HCHO, HCOOH, CH ₃ OH and CH ₄ neg.	
0.1	48	Cathode gas - 0.09% CO Anode gas - 0.5% CO CH ₄ , CH ₃ OH, HCHO neg.	
0.05	48	Cathode gas - 0.05% CH ₄ , 0.23% CO Anode gas - 0.02% CH ₄ , 0.15% CO CH ₃ OH, HCHO, HCOOH neg.	
0.13	48	Cathode gas - 0.007% CH ₄ , 0.22% CO Anode gas - CH ₄ neg., 0.40% CO	Blank run
0.02	48	Cathode gas - 0.075-0.12% CO Anode gas - 0.08% CO CH ₃ OH, HCHO, HCOOH Neg.	
0	48		Cell would not conduct

Tests with anisole as a solvent also showed insufficient conductivity for electrolysis. The salts tried in Runs 166a-166e were LiCl , Li_2SO_4 , NaCl , Na_2SO_4 and MgSO_4 . The tests were made under CO_2 pressure in the pressure cells.

An acetone- LiCl catholyte was tested in Runs 162-165 at 0°C , 30°C and 75°C . CO and CH_4 were found in the gas phase at all three temperatures. A blank cell, using helium as the pressurizing gas, yielded 150 ppm CH_4 and 440 ppm CO after 9 hours electrolysis at 0.5 amp. These results indicate CO and CH_4 were produced by reaction of the catholyte solvent.

A BeCl_2 -ether catholyte at a mercury cathode was tried in Run 160 and 161. The runs were made at 1 atm CO_2 . Considerable water permeated the membrane from the anode during Run 160, but the electrolysis was continued as Run 161 with more water added to the catholyte. No reduction products were found at the end of the electrolysis.

A LiCl -pentanone catholyte system was used for Run 167. This cell exhibited poor conductance characteristics and results were negative after 46 hours electrolysis at 0.003 amp.

Carbon monoxide was found in the gas phase of the pyridine- LiCl cell (Run 168). Samples taken from the anode showed 0.5% CO in contrast to 0.09% CO found at the cathode. The 5 1/2 factor of CO at the anode to the amount at the cathode indicates CO was not formed by CO_2 reduction. A deposit on the lead cathode resulted in gas evolution with water, showing lithium probably was deposited on the electrode during electrolysis without the desired reducing effect on the CO_2 in solution.

Propylene carbonate was used as the solvent for LiCl in Run 170. This cell produced a cathode and anode gas concentration of 0.08% CO . No methane was formed and the equal amount of CO at the anode indicates CO is not the product of CO_2 reduction.

A cell using acetonitrile as the catholyte solvent showed some promise when the cathode gas phase of Run 169a contained more CO and CH_4 than was found at the anode. A blank run resulted in a trace of CH_4 (~ 70 ppm) at the cathode and twice as much CO at the anode (0.40%) than at the cathode (0.22%).

DISCUSSION OF RESULTS AND FUTURE WORK

The use of organic solvents and cation exchange membranes was suggested by two possible reduction mechanisms: an increase in the hydrogen discharge potential at the cathode; and the possible reducing action on CO_2 by an active metal such as lithium or beryllium electrodeposited on a cathode surface.

In the organic solvent-cation exchange membrane systems the current is transported from the aqueous anolyte by the positive hydrogen ion by transfer across the cation exchange membrane. Hydrogen ion concentration in the organic catholyte is theoretically maintained at a low level and the hydrogen discharge potential is increased considerably by the absence of excess hydrogen ions. However, up to 7% water was found in the organic catholytes at the conclusion of the runs, indicating water is permeable to the membranes to a considerable extent, and the anhydrous condition necessary to maintain the high discharge potential was not obtained during the course of the experimental runs.

The reducing action of an active metal deposited at a cathode was demonstrated by the reduction of formic acid by beryllium at a mercury cathode.⁷ In another example of this reducing action, lithium metal deposited at the cathode during the electrolysis of molten lithium carbonate is the basis for an electrolytic method of converting carbon dioxide to oxygen.⁸ This system is anhydrous and the electrolysis is carried out at 550°C .

The lithium chloride-pyridine system used in Run 168 resulted in an active deposit at the cathode believed to be lithium; however, water was also present in the catholyte. It is possible that the lithium at the cathode is not reactive, even to the water in the catholyte, because of cathodic protection.

Work will continue on the organic solvent systems. The lithium chloride-pyridine system will be tried using a pulsating current in order to eliminate cathodic protection periodically. This cell will also be tried at a higher temperature, and attempts will be made to maintain the catholytes at anhydrous conditions.

A method for maintaining separation of the gas products using differential pressure switches will be tried. Catalytic activity will be investigated by adding Raney nickel to the catholytes of operating cells.

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